CHARACTERIZATION OF COATING MICROSTRUCTURE USING LASER SCANNING CONFOCAL MICROSCOPY

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Introduction

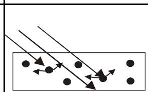
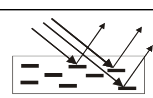
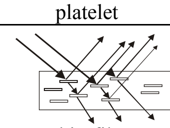
The appearance of coating materials depends on the physical attributes of the object's interaction with light. These physical attributes include the light source, the angle of illumination, the viewing angle, and the optical reflectance properties of the coating system resulting from its surface topography and subsurface microstructure. Identification and characterization of the microstructure of a coating are crucial for relating the microstructure to the optical reflectance properties and for predicting the appearance of a coating from its microstructure and its constituents, and for predicting changes that occur as a coating weathers.

In the past, the attributes of subsurface microstructure of coating materials, such as pigment size, dispersion, and spatial distribution, have often been characterized using destructive techniques such as scanning electron microscopy (SEM) or transmission electron microscopy (TEM) on sectioned samples. These destructive microscopic techniques usually require a great deal of sample preparation, and experimental artifacts might be introduced during the process. Laser scanning confocal microscopy (LSCM) is known for its non-contact and non-destructive features, and has been used extensively in the biomedical arena. [1] In this paper, we will demonstrate that LSCM is a powerful tool for characterizing microstructure of pigmented coatings. The microstructure determined using laser scanning confocal microscopy is presented and compared to the corresponding optical reflectance data obtained from NIST's bidirectional reflectance distribution function (BRDF) instrument. [2]

Experimental

Materials. A series of samples varying in their microstructural properties (e.g. pigment size, dispersion, and spatial distribution) was used to investigate the relationship between the nature of the microstructure and the optical reflectance properties of the coatings. Three common types of pigments – TiO_2, metallic, and pearlescent pigments, were used in this study. The primary (first-order) interaction between light and the pigments are summarized in Table 1. TiO_2 pigmented coatings were prepared in the Building Materials Division at NIST. TiO_2 pigments (from Millennium Co.[3]) were well dispersed into an acrylic urethane binder, and were cast on release paper or glass substrates using drawdown blade or spin-casting techniques. Metallic and pearlescent pigmented coatings were prepared on aluminum substrates and provided by Du-Pont chemical company.[3] Note that PVC denotes the pigment volume concentration in the coating.

Table 1. Optical Principles of TiO_2, metallic, and pearlescent pigments

Pigment Type	**Particle** TiO_2	**Metallic** Aluminum flake	**Pearlescent** TiO_2 coated mica platelet
Optical Principle of Pigments (first-order)	 Scattering	 Reflection	 Thin-film Interference
Appearance	Independent of geometry	Depends on viewing angle	Depends on illumination and viewing angle

Instrumentation. A Zeiss model LSM510[3] laser scanning confocal microscope was employed to characterize the microstructure of the coatings. LSCM utilizes coherent light and collects light exclusively from a single plane (a pinhole sits conjugated to the focus plane) and rejects the out-of-focus-plane light. The wavelength, numerical aperture of the objective, and the size of the pinhole dictate the resolution in the thickness or axial direction.[1] By moving the focus plane, single images (optical slices) can be put together to build up a three dimensional stack of images that can be digitally processed. In this paper, LSCM images in depth profile or intensity profile presentations are images of overlapping optical slices (a stack of z-scan images) with each z-step from 0.5 µm to 1 µm depending on the pigment size and distribution. Acquisition of a typical optical slice takes less than 8 seconds. Various locations of the sample can be scanned in minutes and with two interchangeable incident wavelengths (543 nm and 488 nm).

In-plane bidirectional reflectance distribution function (BRDF) of the metallic and pearlescent pigmented coatings were performed using the NIST spectral tri-function automated reflectance reflectometer (STARR). Details of the instrumentation and measurement capabilities are described elsewhere.[2]

Results and Discussion

Image and data processing from LSCM results were compared to optical scattering reflectance measurements and are presented in the following subsections for TiO_2, metallic, and pearlescent pigmented coatings.

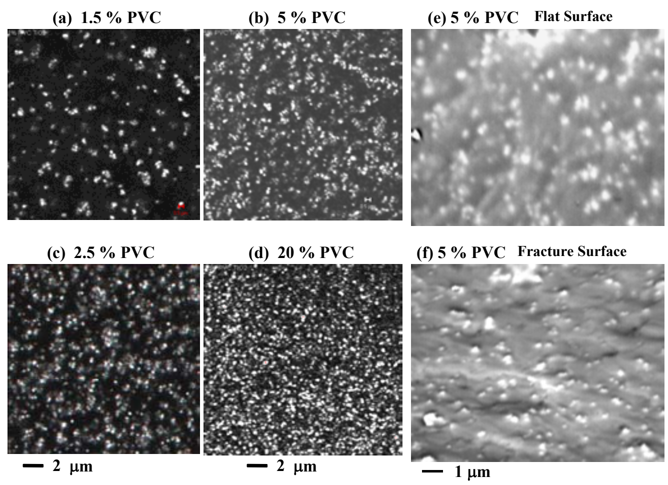


Figure 1. (a)-(d) LSCM images of TiO_2 pigments in an acrylic urethane binder for four different pigment volume concentrations (PVC). (e)-(f) Backscattering SEM images of 5 % PVC samples.

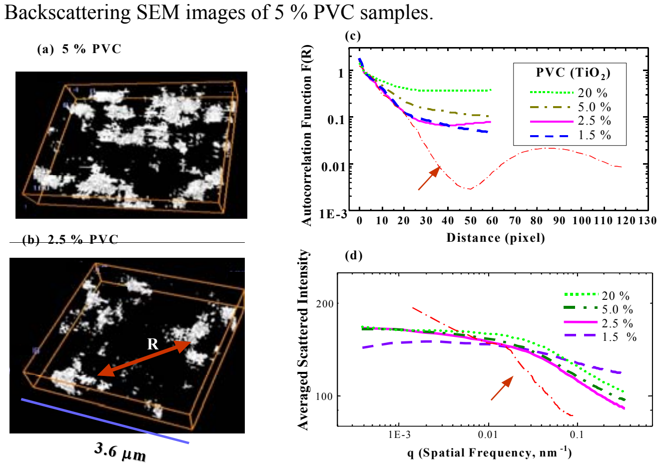


Figure 2. (a)-(b) 3D reconstruction images for the 5 % and 2.5 % PVC TiO_2 pigmented samples. (c) Autocorrelation function F(R), and (d) circularly averaged scattered intensity obtained from Fast Fourier transformation (FFT) of LSCM images in Fig. 1 for four different PVC samples.

(1) TiO_2 Pigmented Coatings. Fig. 1a-d show LSCM images of TiO_2 pigments in an acrylic urethane binder for four different pigment volume concentrations. The LSCM technique provides a powerful visual aid for charactering the pigment or cluster size and dispersion as a function of PVC. However, due to the finite depth and lateral resolution (≈450 nm in this case) limited by the numerical aperture and wavelengths of the LSCM system, it is difficult to measure and determine a particle size smaller than 450 nm. Thus, backscattering SEM measurements were carried out on the 5 % PVC sectioned samples (flat and fracture surfaces coated with gold) to determine the pigment particle size and spatial distribution in both flat (Fig. 1e) and fracture surfaces (Fig. 1f). The size of a single TiO_2 pigment was about 300 nm, which is consistent with data provided by the manufacturer. In contrast to a typical SEM measurement, LSCM can easily provide adequate representations for describing and characterizing the pigment dispersion for a non-destructive, fast measurement.

In addition to measuring the particle (or cluster) size and particle-particle distribution directly from LSCM images, we can reconstruct a three-dimensional (3D) microstructure using a 2D image (a single optical slice).[4] Fig. 2a-b show the 3D reconstructed microstructure for 5 % and 2.5 % PVC samples. The autocorrelation function F(R) was calculated for these four PVC samples and is presented in Fig. 2c, which also includes F(R) of the LSCM measurements on the sample containing NIST SRM 1690 (900 nm) polystyrene latex (PSL) spheres using the same technique. The important parameters, such as the pigment or cluster size and the location in 3D, can be obtained and used for scattering theory modeling to predict the optical properties of the coatings. Further image analysis using Fast Fourier transformation (FFT) of LSCM images (Fig. 2d) can be used to link the measured microstructure images to scattering measurements, such as small angle neutron and light scattering.

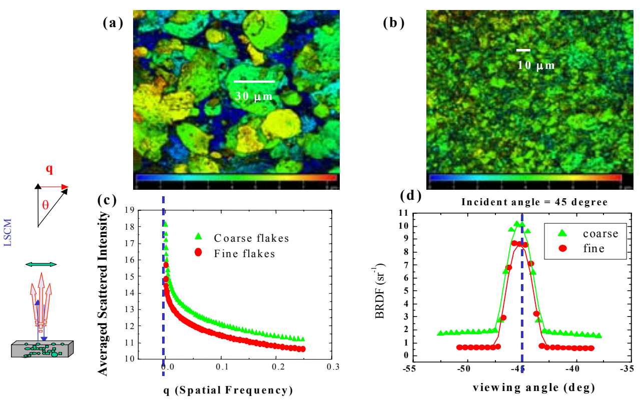


Figure 3. LSCM images of gray, aluminum-flake pigmented coatings having same PVC but containing different pigment sizes, coarse (a) and fine (b). (c) and (d) show the FFT-scattered intensity and BRDF data of these two samples. The measurement uncertainties are less than ± 0.5 % (relative expanded uncertainty, k=2) and smaller than the size of the symbols used in the graphs.

(2) Metallic pigmented coatings. The most important metallic pigments are aluminum (Al) flake pigments. A wide variety of the flake size is available, and the orientation of flakes depends on treatments of the flakes and processing conditions. To investigate the relationship between the optical properties of components of a coating system, and the coating microstructure with the optical scattering of light reflected from the coating, we have selected two gray, Al-flake pigmented coatings having the same PVC but containing different pigment sizes − one containing relatively coarse and the other containing relatively fine Al flakes. The sample having coarse flakes (Fig. 3a) exhibits a grainy finished texture and the sample having fine flakes exhibits a smoother finish in the visual inspection. From the LCSM results, most of Al flakes orient within the film parallel to the surface of the coating. Optical reflectance data (BRDF) were measured for these two samples at 45° specular geometry using STARR and are presented in Fig. 3d. To understand the interaction between light and Al flakes, the circularly averaged scattered intensity from FFT data of LSCM images (Fig. 3c) were analyzed and compared with BRDF data. FFT data are consistent with BRDF data in both specular and off-specular intensities. This result implies that LSCM images can be used to predict scattering properties. This application will be useful for examining and characterizing the determinant microstructure of products under different processing conditions and for predicting the appearance of the final product using some microstructure-reflectance models.

(3) Pearlescent pigmented coatings. Pearlescent pigments consist of a transparent mica platelet coated with a layer of TiO_2 or other thin film. Due to the light interference feature of the pigment, the observed pigment size and distribution are dramatically different under different illumination conditions, as demonstrated in Fig. 4a. Fig. 4 shows LSCM images of a green pearlescent coating under different laser wavelengths in the same location. More pigments are observed under green light than under blue light. Moreover, the shape and relative distance in depth are different. To obtain a real image of the pigment size and distribution, an optical microscopy (OM) image using white light is also presented here. It is clear that the appearance of this pearlescent pigmented coating strongly depends on the illumination as well as viewing angles. Optical reflectance measurements using STARR on the pearlescent pigmented sample, which includes lightness and chromatics as a function of illumination and viewing angles, will be compared with the LSCM microstructure results using two laser wavelengths and different tilt angles of samples. In addition to the information on the pigment size and distribution, the film thickness of the coated TiO_2 layer can be deduced from the interference fringes in the intensity profile, as shown in Fig. 4c-d.

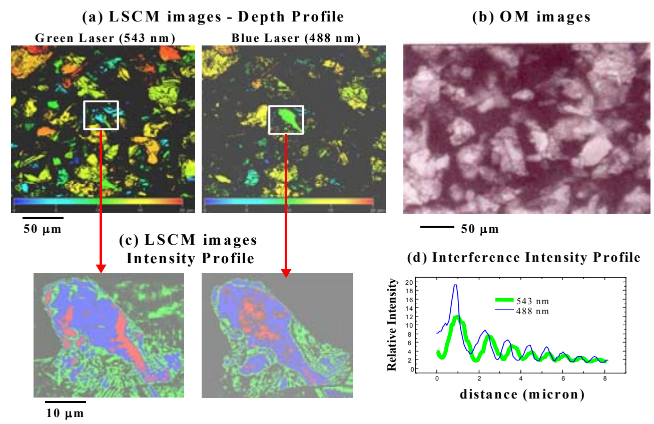


Figure 4. (a) LSCM images for a pearlescent sample at two different illuminated wavelengths. (b) The optical microscopy image for the same sample. (c) High magnification of the center region in intensity profile presentation for two different wavelengths. (d) A representative intensity plot for the interference fringes.

Summary

We have demonstrated that laser scanning confocal microscopy is a powerful technique for characterizing coating microstructure. The microstructure of pigmented coatings was accurately and rapidly obtained using LSCM. Using the FFT image analysis, the microscopic data can be related to the optical scattering measurements. In addition, real-space topography data or 3D reconstruction images can be used for scattering modeling to calculate the optical properties, and compared to the measured BRDF data.

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References

(1) Corle, T.R.; Kino, G.S. "*Confocal Scanning Optical Microscopy and Related Imaging Systems*" *Academic Press* **1996**.

(2) Barnes, P.Y; Early, E.A; Parr, A.C. *NIST Special Publication* **1998**, 250-*28*.

(3) Certain instruments or materials are identified in this paper in order to adequately specify experimental details. In no case does it imply endorsement by NIST or imply that it is necessarily the best product for the experimental procedure.

(4) Bentz, D.P.; Martys, N.S. *Transport in Porous Media* **1994**, 17, 221.